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Optical dynamics of excitons in *J* aggregates of a carbocyanine dye

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Results of temperature and wavelength dependent fluorescence lifetime and accumulated photon-echo experiments on the *J* aggregate of the dye 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-di(4-sulfobutyl)-benzimidazolocarbocyanine (TDBC) in an ethylene glycol/water glass are reported. Additionally, the temperature dependent relative fluorescence quantum yield was determined. Using two-color pump–probe spectroscopy, the intersite correlation of the frequency disorder and the size of the coherence domains were estimated. Both the phase and the population relaxation times are frequency dependent in the echo and the single-photon-counting experiments. The dependence of the fluorescence lifetime on detection wavelength is restricted to temperatures below 80 K, indicating a temperature activated process. From our experiments and by comparison with previously published results we conclude that the dispersive nature of both the dephasing and the depopulation is caused by intraband relaxation processes. At higher temperatures this wavelength dependence vanishes due to thermalization. The temperature dependence of the relative fluorescence quantum yield of TDBC is equal to the one of pseudoisocyanine (PIC). Using a motional narrowing model for disordered molecular aggregates with consideration of intersite correlation, at 1.5 K, the two-color pump–probe experiments indicate a very high correlation in the frequency disorder in TDBC *J* aggregates with a correlation length of several hundred molecules. From pump–probe experiments the delocalization length of the exciton is determined to be between 30 and 45 molecules at 1.5 K. © *1995 American Institute of Physics.*

I. INTRODUCTION

J aggregates are assemblies of molecules with coherently coupled transition dipole moments with a very intense, narrow, and, with respect to the monomer-band, redshifted absorption band (*J* band). They have attracted considerable attention lately as a system bridging the gap between the physics of single molecules and structurally ordered crystals, therefore being of fundamental importance for the general understanding of molecular and solid-state physics. Also, there is a variety of possible applications of *J* aggregates, for example, in the field of optical communication because of their high nonlinear optical coefficients.[1] Today, they are widely used as spectral sensitizers for photographic materials.[2] The possibility of mirrorless optical bistability in molecular aggregates was studied theoretically by Gusev.[3] In biology, aggregates are of general interest since most photobiological processes, including photosynthesis, rely on aggregates for energy or charge transfer processes. A dye structurally very similar to the one investigated in this paper was used as a quantitative indicator of membrane potential.[4] *J* aggregates may also serve as model systems for other applications such as the development of molecular wires.[5] Most technological applications of molecular aggregates are based on the size enhancement of their optical properties caused by the excitonic nature of electronic excitations in the aggregates.

After their characteristic spectra were first observed by Jelley[6] and Scheibe[7] in the mid-thirties, *J* (or Scheibe) aggregates have been the subject of a large number of investigations which, during the last few years, concentrated on laser-spectroscopical techniques such as fluorescence lifetime,[8–10] spectral hole-burning,[9,11,12] photon-echo,[11,13] pump–probe,[14] and light-scattering experiments.[8,15]

Because it is the dye for which *J* aggregation was first observed, pseudoisocyanine (PIC) is the most often investigated and best known *J*-aggregating dye and almost all theoretical models were designed for and tested with PIC. The static aggregate absorption spectrum of PIC was modeled by Scherer and Fischer[16] using a mean-field approximation and assuming the aggregate to be a linear chain with each unit cell containing two molecules. Knapp[17] showed that the unusual sharpness of the transition from the ground state to the first excited aggregate state can be explained by motional narrowing, i.e., an averaging over local inhomogeneities, if one assumes that there is no correlation of this inhomogeneous disorder between neighboring molecules of the aggregate. Although Knapp[17] in his work did consider the effect of intersite correlations, it was not possible to experimentally measure it and until recently it has been assumed that the disorder was indeed uncorrelated. Knoester[18,19] showed that nonlinear optical experiments like two-color pump–probe measurements are an appropriate means by which both the degree of correlation and the magnitude of the disorder can be measured. This approach was recently applied to aggregates of PIC,[20] which indicated that the transition energies of

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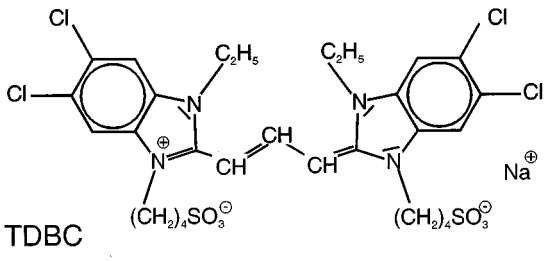

FIG. 1. Molecular structure of the dye 5,5′,6,6′-tetrachloro-1, 1′-diethyl-3,3′-di(4-sulfobutyl)-benzimidazolocarbocyanine (TDBC).

neighboring molecules within PIC aggregates are highly correlated. The understanding of the optical dynamics of PIC has made great progress during the last decade[11,13,15,21–23] and early discrepancies in the reported fluorescence lifetimes were eliminated when it could be shown that the measured lifetimes are shortened by exciton–exciton annihilation if the excitation intensity is too high.[24–26] A special feature of *J* aggregates is the decrease of the fluorescence lifetime with decreasing temperature.[13,27] This unusual behavior was simulated by Spano and Mukamel[28] with a model in which it results from localization of the excitons (exciton–phonon scattering). Because the fluorescence lifetime is inversely proportional to the number of coherently coupled molecules, it decreases with decreasing temperature. A very general numerical simulation of the optical properties of linear molecular aggregates with diagonal and off-diagonal disorder including all dipolar couplings was developed and applied successfully to PIC by Fidder *et al.*[23]

The dye investigated for this paper is 5,5′,6,6′- tetrachloro-1, 1′-diethyl-3,3′-di(4-sulfobutyl)-benzimidazolocarbocyanine (TDBC), which is known to easily form *J* aggregates.[9,10,29–31] Its structure is shown in Fig. 1. TDBC is, contrary to PIC, not sterically hindered and should therefore have an almost planar structure. This was shown by x-ray structure analysis[32] for a dye similar to TDBC, in which there are ethyl groups instead of the sulfobutyl groups.

At room temperature and in aqueous solution, TDBC forms *J* aggregates at very low concentrations (down to 10^{-5} mol/ℓ) with an absorptivity in the peak of the *J* band of up to 600 000 cm^2/mmol (per molecule in the *J* aggregate), by far exceeding the absorptivities of other known *J* aggregating dyes (PIC: 250 000 cm^2/mmol per molecule in the aggregate[33]). At concentrations higher than about 5×10^{-5} mol/ℓ in water, almost all TDBC molecules are bound in *J* aggregates and the monomer concentration is too low to be detected by conventional spectrophotometric techniques. Contrary to PIC, TDBC is not known to form dimers or *H* aggregates under any environmental conditions, making the interpretation of spectroscopic data easier.

The sodium salt of TDBC was first investigated by Herz[29] by room temperature steady-state absorption experiments. From the mass-action relations he computed an association number of four for the TDBC *J* aggregates. However, this result could not be confirmed by Makio *et al.*[30] who did similar experiments and found an association number of eight. The circular-dichroism (CD) spectra of TDBC measured by Honda *et al.*[34] suggest the growing of the *J* aggregates of TDBC on aging, but no further experiments with TDBC were done because the time dependent changes in the CD spectra were too complicated. Recently, Lindrum *et al.*[9] reported on influences of the microenvironment on the fluorescence decay and hole-burning experiments in the TDBC *J* band. They found that no persistent holes could be burnt in the *J* band of TDBC indicating that the potential barriers for conformational changes, which are assumed to be the relevant hole-burning process in the case of PIC *J* aggregates,[35] are too high to allow efficient hole burning. The TDBC *J* aggregate dynamics in liquid solution at room temperature was just recently investigated by femtosecond nonlinear optical experiments, which indicated that the dynamics of TDBC aggregates in water has to be described in a non-Markovian way.[36] Also, the population decay time was measured by a population-grating scattering experiment at room temperature.[36] In the same paper, the room temperature exciton delocalization length was determined to be about 16 molecules by pump–probe experiments.

In this paper we investigate the low temperature dynamics of TDBC and compare the results with the ones previously published for other *J* aggregating dyes. The purpose of our investigations is to apply ideas and models developed for PIC to other *J* aggregating dyes in order to get a more general understanding of the primary photophysical processes in *J* aggregates. We present new results obtained by static and time-resolved optical spectroscopy and by accumulated photon-echo and two-color pump–probe experiments in the *J* band of TDBC.

II. EXPERIMENT

Samples were made from a 1.8×10^{-3} mol/ℓ stock solution of TDBC in doubly distilled water by dilution with ethylene glycol and water, resulting in solutions of 4.5×10^{-4} and 9×10^{-5} mol/ℓ in a 1:1 mixture of ethylene glycol and water. No monomers were observed in the absorption spectra of any of the samples used for the experiments.

For fluorescence experiments (static and time-resolved) the absorbance of the sample was kept below 0.2 (typically 0.1) to avoid reabsorption. This was done by filling the sample solution in micrometer cuvettes or between thin glass plates. The layer thicknesses were between 5 and 30 μm. For the accumulated photon-echo experiments, cuvettes with a thickness of up to 100 μm were used (resulting in a typical absorbance of 0.7). The samples were mounted on a copper sample holder, quickly cooled down to liquid nitrogen temperature (~15 min.) and then cooled down to 1.5 K over a period of about 1 h. Experiments at higher temperatures were done by slowly heating the cryostat to the desired temperature.

The accumulated photon-echo experiments were performed the usual way[37,38] using a 94 MHz train of stochastic pulses obtained from a dye laser (Coherent CR599, dye: R6G) pumped by a mode-locked Ar^+ laser (Coherent Innova 99). For the two-color pump–probe experiments,[14] two synchronously pumped dye lasers with a spectral bandwidth of 9 cm^{-1} and an excitation density of 10^{10} photons cm^{-2} pulse $pair^{-1}$ were used. For the time-correlated single-photon-

counting experiments, the dye laser additionally was cavity dumped at a rate of 94 kHz. The excitation density usually was 10^{12} photons cm^{-2} $pulse^{-1}$. By variation of the laser power and comparison of the measured lifetimes it was ascertained that the fluorescence lifetimes were not influenced by exciton–exciton annihilation. The excitation wavelength for the time-resolved fluorescence experiments was 562 nm. The fluorescence from the time-resolved experiments was detected through a Zeiss M4 QIII prism monochromator with a Hamamatsu microchannel plate detector (1534-U01V), yielding an overall system response time of about 30 ps (FWHM). Static fluorescence was detected through a conventional grating monochromator (Spex). The lifetime experiments were done in samples showing resonant fluorescence and in samples with a double fluorescence band (see below). However, within the experimental error, no deviations in the measured fluorescence lifetimes were found for the different samples.

The fluorescence quantum yield at different temperatures was measured by static absorption and fluorescence experiments on spectrometers from Shimadzu (spectrophotometer UV-240 Graphicord and spectrofluorometer RF-540, respectively). Since the absorption spectrum does not change with temperature below 150 K, except for a slight wavelength shift, the relative fluorescence quantum yield below 150 K was simply determined by integration of the fluorescence emission spectrum. For the fluorescence emission spectra, the samples were quickly cooled to about 5 K and then slowly heated to the desired temperatures. The sample position and the settings of the spectrofluorometer were left unchanged during the experiments. The maximum absorbance of the samples used for the quantum yield measurements was 0.03 and no monomers were observed in the absorption spectra. The excitation wavelength for the fluorescence spectra was 500 nm with an excitation bandwidth of 10 nm.

III. FUNDAMENTALS

Generally, the appearance of the *J* band is explained by treating the aggregate as a chain of coupled two-level systems. If one allows only one excitation per aggregate, this assumption leads to the following Hamiltonian for the aggregate:[23]

$$H=\sum_n (\langle \epsilon \rangle + D_n)|n\rangle\langle n| + \sum_n \sum_{m,m\neq n} J_{nm}|m\rangle\langle n|. \qquad (1)$$

Here, $|n\rangle$ is the state of the system where the nth molecule is excited, $\langle \epsilon \rangle$ is the average molecular excitation energy, D_n is the inhomogeneous energy offset of the nth molecule, and J_{mn} is the interaction energy between molecules m and n. It was shown that in the case of large one-dimensional aggregates with parallel alignment of the dipoles, assuming the intermolecular interaction to be of dipolar nature, the total width of the exciton is about 4.2 $|J|$[23] (J=interaction energy between two molecules at the average nearest-neighbor distance). For positive *J*, only transitions to the upper (high energy) end of the exciton band are allowed (resulting in an absorption band called *H* band). The so-called *J* band appears for negative *J*, for which only transitions to the bottom (low energy) region of the exciton band are allowed. In both cases only one single peak in the absorption spectrum is observed and additional peaks only appear if the transition dipoles in the aggregate are not parallel to each other[39] or if several different types of aggregates (resulting in different values for *J*) are present in the sample.

Fidder *et al.*[23] reported on the effects of disorder (diagonal and off-diagonal) on the optical properties of molecular aggregates. Assuming the disorder of the oscillator frequencies to be completely uncorrelated, Knapp[17] showed that for circular aggregates, a Gaussian distribution of oscillator frequencies is narrowed by a factor of $N^{-1/2}$, where N is the number of molecules over which the excitation is delocalized. This model is quite powerful in explaining many effects of disorder on excitonic properties, but it cannot provide quantitative results. A detailed discussion of the effect of correlated and uncorrelated disorder on the bandwidth was recently presented by Knoester, showing that the narrowing of the *J* band may be much less than $N^{-1/2}$ if the disorder is correlated.[18] Knoester also showed that the degree of intersite correlation in the frequency disorder in molecular aggregates can be determined by two-color pump–probe experiments. In these experiments, a bleach at the excitation wavelength and an induced absorption blueshifted to the bleach are observed. The induced absorption is attributed to one-exciton to two-exciton transitions[14] and the energy difference $\Delta_{\mathrm{abs,bl}}$ between this peak and the bleach is related to the detuning of the pump frequency ω_1 from the center of the *J* band Ω_1^0 according to

$$\Delta_{\mathrm{abs,bl}} = \alpha(\omega_1 - \Omega_1^0) + (\Omega_2^0 - \Omega_1^0) \qquad (2)$$

(notation as in Ref. 18). Here, Ω_k^0 is the frequency of the one exciton in the kth level of the exciton band in the homogeneous system (no disorder) given by

$$\Omega_k^0 = \omega_0 + 2J\cos\left(\frac{\pi k}{N+1}\right), \qquad (3)$$

and α is a function of the correlation length l_0 of the disorder in the transition frequencies of the molecules within one chain.[18] So, if $(\Omega_2^0 - \Omega_1^0)$ can experimentally be determined [by measuring $\Delta_{\mathrm{abs,bl}}$ when pumping at the peak of the absorption band $(\omega_1 = \Omega_1^0)$], one can straightforwardly calculate the delocalization length N using Eq. (3). In a first order approximation $(N \gg 1)$, one obtains

$$N \approx \sqrt{\frac{-3\pi^2 J}{\Omega_2^0 - \Omega_1^0}} - 1. \qquad (4)$$

J can be estimated from the frequency shift between the *J* band and the monomer band in the absorption spectrum.

The fluorescence lifetime of a *J* aggregate depends on its size and geometrical structure. According to the exciton model for linear aggregates by McRae and Kasha,[40] the aggregate transition dipole moment is enhanced by a factor of $N^{1/2}$ compared to the monomer transition dipole moment. Together with the Strickler–Berg relation,[41] in which the radiative lifetime is proportional to the square of the transition dipole moment, this leads to an overall increase of the radiative rate of aggregates compared to the monomer's radiative

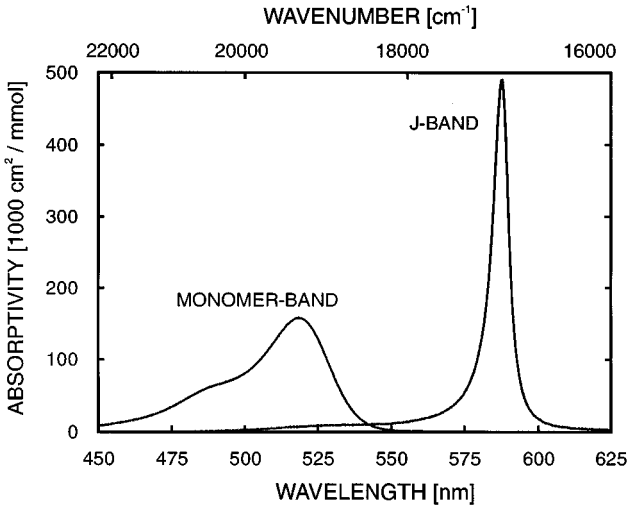

FIG. 2. Monomer band of TDBC (in methanol, concentration 3.4×10^{-5} mol/ℓ) and *J* band of TDBC (in bidistilled water, concentration 1.4×10^{-4} mol/ℓ) at room temperature.

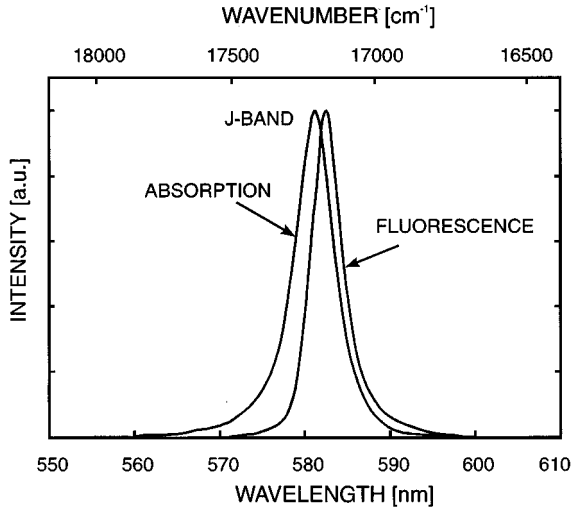

FIG. 3. Low temperature (5K) absorption and resonance fluorescence emission spectra of TDBC *J* aggregates (solvent: 1:1 mixture of ethylene glycol and water, concentration: 4.5×10^{-4} mol/ℓ).

rate by a factor of N. However, this does not take into account that in the case of large linear aggregates, also in-band states ($k>1$) can be excited in the absence of disorder,[17] leading to a dilution of the oscillator strength over many levels in the exciton band. In this case, the lowest energy level ($k=1$) still contains most of the oscillator strength (81%), resulting in an increase of the radiative rate for large linear aggregates by a factor of (0.81 N). This relation is based on the assumption that dephasing is absent,[42] which, at low temperature, is justified.

The population relaxation time T_1 of the excited state and the homogeneous linewidth $(\pi c T_2)^{-1}$ are related to each other according to

$$\frac{1}{T_2}=\frac{1}{T_2^*}+\frac{1}{2T_1}, \tag{5}$$

where T_2 is the dephasing time (measured by photon-echo experiments) and T_2^* describes the pure dephasing caused by fluctuations of the electronic eigenstates, which are expected to disappear at low temperature.

IV. RESULTS AND DISCUSSION

A. Steady-state spectroscopy

Figure 2 shows the monomer absorption band of TDBC, measured in methanol, and the *J* band of TDBC in doubly distilled water at a concentration of 1.4×10^{-4} mol/ℓ, both measured at room temperature. In methanolic solution the monomer peak absorptivity was determined to be 160 000 $\pm$5000 cm^2/mmol, independent of concentration. As shown in Fig. 2, the aggregate absorption band is shifted to lower energies by about 2270 cm^{-1} and its linewidth decreases from 1200 cm^{-1} (FWHM) to 240 cm^{-1} (FWHM). The width of the monomer absorption band without vibrational shoulder at room temperature is $\sim$850 cm^{-1}. As shown by Fidder *et al.*,[23] taking into account all dipolar interactions between the molecules in a large aggregate, the lower edge of the exciton band is located at $E=-2.403\ |J|$, where $E=0$ is the monomer transition energy and J the interaction energy between two molecules at the average nearest-neighbor distance. Since the *J* band is located at the lower edge of the exciton band, at low temperature one obtains $J\approx-840$ cm^{-1} for TDBC. However, this is not taking into account other possible reasons for shifts like the van der Waals shift, so 840 cm^{-1} is only an upper limit for $|J|$. The fact that only one aggregate band is observed in the spectrum indicates that the transition dipoles in the aggregate are parallel to each other.[39]

The absorption and the fluorescence emission of the *J* band of TDBC at low temperature are shown in Fig. 3. The maximum of the absorption is located at 582 nm. We note that a considerable blueshift with decreasing temperature is observed at temperatures above the glass transition ($\approx$200 K) of the 1:1 mixture of ethylene glycol and water, but at lower temperatures the changes in the absorption spectrum of TDBC are small. The linewidth of the absorption *J* band at low temperatures is 160 cm^{-1}, one third less than at room temperature. The apparent Stokes shift of the fluorescence emission of the TDBC *J* aggregate is very small ($\leqslant$1 nm). Changes with temperature in intensity and bandwidth of the TDBC fluorescence emission are considerable, even at low temperatures. In some cases, even two different fluorescence bands are observed, one in resonance (peak at 583 nm at 1.5 K) and one off resonance (peak at 589 nm at 1.5 K). However, the formation of these bands strongly depends on sample preparation and is not reproducible.

From the measured temperature dependence of the absorption and fluorescence spectra the temperature dependence of the relative fluorescence quantum yield of TDBC *J* aggregates was determined (Fig. 4). For the plot in Fig. 4 we assumed the absolute quantum yield to be 1 at 1.5 K. Since below 150 K only small changes in the absorption spectrum are observed, the fluorescence quantum yield was determined simply by integrating over the fluorescence emission

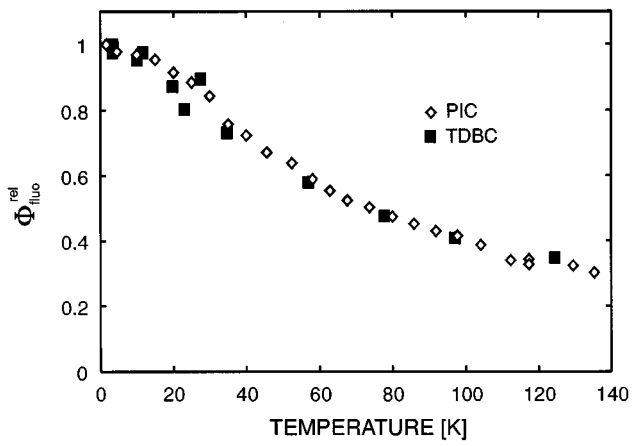

FIG. 4. Temperature dependence of the relative fluorescence quantum yield $\Phi_{\text{fluo}}^{\text{rel}}$ of TDBC *J* aggregates (solvent: 1:1 mixture of ethylene glycol and water, concentration: 4.5×10^{-4} mol/ℓ) and PIC (PIC data taken from Ref. 43).

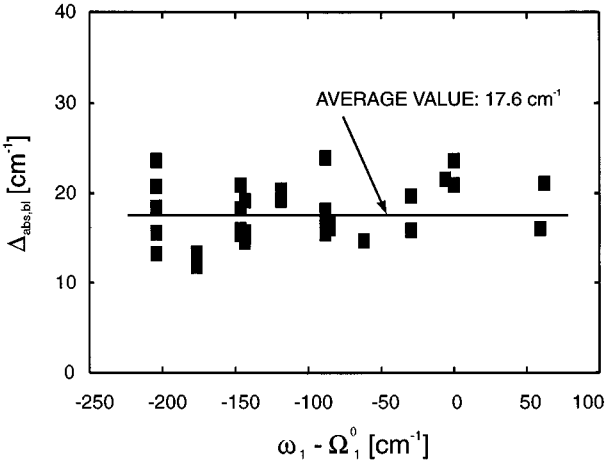

FIG. 6. Dependence of the energy difference $\Delta_{\text{abs,bl}}$ between the bleach and the induced absorption on the frequency detuning of the pump beam from the *J*-band peak $(\omega_1-\Omega_1^0)$ for TDBC at 1.5 K (solvent: 1:1 mixture of ethylene glycol and water, concentration: 4.5×10^{-4} mol/ℓ).

band. For measuring the quantum yields, a sample showing resonant fluorescence only was used. An interesting observation is that the measured temperature dependence of the relative fluorescence quantum yield $\Phi_{\text{fluo}}^{\text{rel}}$ of TDBC *J* aggregates is identical to the one measured for PIC *J* aggregates (Fig. 4, PIC data taken from Ref. 43). This might be an indication that the process responsible for this dependence is of a fundamental nature and independent of aggregate structure and composition.

B. Two-color pump–probe spectroscopy

In the two-color pump–probe experiments at 1.5 K, two main features are observed (Fig. 5): First, a narrow bleach and increased absorption signal (marked I in Fig. 5), moving along with the pump wavelength, the increased absorption signal being blueshifted to the bleach at the pump wavelength; second, a broad feature (marked II in Fig. 5) at about

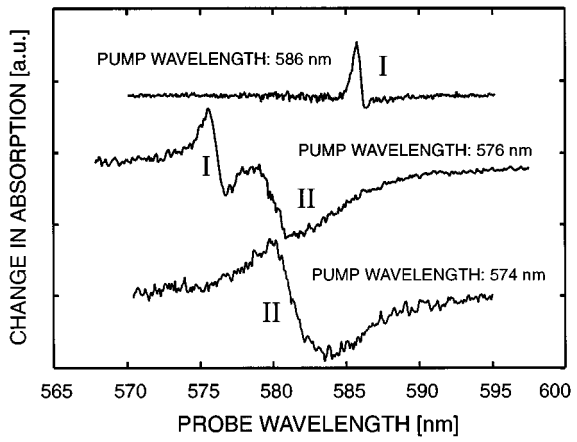

FIG. 5. Pump–probe spectrum for TDBC *J* aggregates at 1.5 K for different pump wavelengths (solvent: 1:1 mixture of ethylene glycol and water, concentration: 4.5×10^{-4} mol/ℓ). The time delay between the pump and probe pulses was 0 ± 10 ps.

constant wavelength with a bleach approximately corresponding to the linear absorption signal, both in position and width, and a blueshifted increased absorption of about equal width. The amplitude of this broad feature depends on the pump wavelength and increases with decreasing pump wavelength.

The narrow feature can be assigned to a bleach at the pump wavelength and a blueshifted absorption due to one-exciton to two-exciton transitions as was shown for PIC.[14] The broad feature, however, is an effect not observed before and may be caused by a redistribution of excitons over the exciton band. This process depends on the possibility of intraband transitions which, at low temperature, only occur to lower energy levels in the exciton band (no thermal excitation). This makes plausible why the broad signal increases for shorter pump wavelengths and completely disappears when pumping in the long wavelength tail of the *J* band (Fig. 5). The broad feature then is caused by the same process that leads to the appearance of the narrow feature, the induced absorption being due to a transition from the one-exciton band to the two-exciton band.

In order to get information on the delocalization length and the intersite correlation in the disorder we plotted the energy difference $\Delta_{\text{abs,bl}}$ between the observed bleach and induced absorption in the narrow feature for small time delays as a function of the detuning of the pump frequency ω_1 from the peak of the *J* band Ω_1^0 (Fig. 6). Similar results were obtained for longer time delays. Fitting the spectra with two overlapping Gaussians and using the energy difference between the peaks of the two fitted Gaussians instead of the experimental peaks would lead to similar results. These indicate a slope α very close to zero and an offset $(\Omega_2^0-\Omega_1^0)$ of 18 ± 5 cm^{-1} (Fig. 6).

From Eq. (4) and $J=-840\pm50$ cm^{-1}, one can calculate the delocalization length *N* of the exciton, independent of the degree of intersite correlation, to be between 30 and 45

molecules at 1.5 K. This is similar to the value of 70 ± 20 found for PIC[20] and only two to three times larger than the delocalization length of 16 molecules found for TDBC *J* aggregates at room temperature.[36] This value for *N* agrees well with results based on other experimental techniques[8,44,45] and, as shown below, our own fluorescence lifetime experiments.

Using the model by Knoester[18] described above, from *N* and α one may calculate the degree of correlation β between the transition frequencies of the molecules within one chain to be very close to 1. The exact value of β, however, could not be determined due to the large spread in the measured values of $\Delta_{\mathrm{abs,bl}}$. In this model, the intermolecular correlation of the transition frequencies in a TDBC *J* aggregate is very high and the correlation length l_0 (defined by $\beta = e^{-1/l_0}$) can be estimated to be several hundred molecules. As shown by Knoester,[18] in the case of high intermolecular correlation between the transition frequencies of the molecules in an aggregate, little or no narrowing of the *J* band compared to the monomer band is expected. The narrowing observed in the case of TDBC in this model therefore would be due to a decrease in amplitude of the disorder (i.e., reduced inhomogeneous broadening of the absorption band), caused by a reduction of the degrees of freedom for the molecules in an aggregate. The very high degree of correlation for TDBC *J* aggregates agrees with the results obtained for PIC where the correlation length l_0 was found to be between 50 and 100 molecules.[20] However, the narrowing of the PIC *J* band is larger than for TDBC. The limited configurational freedom of the first solvation shell in the presence of the ordered aggregate during the freezing process was given as a possible explanation for the narrowing in the case of PIC.

The temperature dependence of the width of the *J* band, however, is not an appropriate indicator for the validity of the model by Knoester. The observed narrowing of the *J* band at low temperature is the same as the narrowing of the origin transition of the monomer band (30%–40% decrease in linewidth when going from room temperature to 5 K), so it could be explained by a reduction of the inhomogeneous broadening. However, the increase in aggregate size by a factor of 2 or 3 would also lead to a narrowing of the *J* band by 30% to 40%, so each of the two effects or a superposition of both may be responsible for the temperature dependent narrowing of the *J* band.

Besides $\Delta_{\mathrm{abs,bl}}$, the width of the induced absorption in the two-color pump–probe spectra, using the model by Knoester, is an indication for the degree of intersite correlation, too. In the case of TDBC *J* aggregates at low temperature, the width is smaller than 35 cm^{-1} for all pump wavelengths used and might be limited by the laser width. This value, less than 22% of the *J* band width at the same temperature, also indicates a large degree of intersite correlation. The model by Knoester[18] for the frequency dependent pump–probe signals in the *J* aggregates of TDBC thus leads to results which are in themselves consistent. However, an independent experiment, aimed at testing the conclusion that in this aggregate the correlation length amounts to hundreds of molecules, remains mandatory.

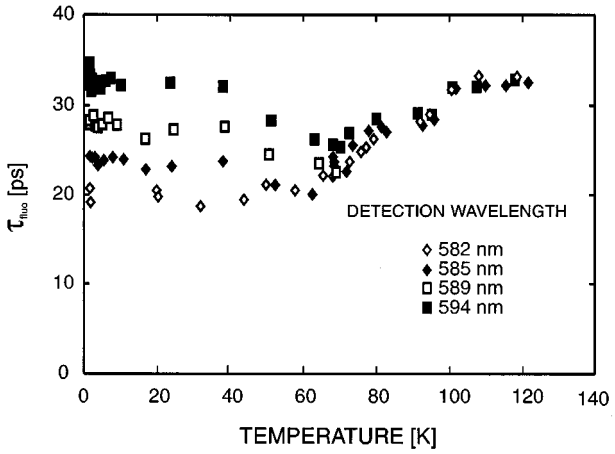

FIG. 7. Temperature and detection wavelength dependence of the fluorescence lifetime of TDBC *J* aggregates (solvent: 1:1 mixture of ethylene glycol and water, concentration: 9×10^{-5} mol/ℓ; emission wavelengths: ◇: 582 nm; ◆: 585 nm; □: 589 nm; ■: 594 nm).

C. Time-resolved fluorescence

From Fig. 7 it is evident that below 80 K the fluorescence lifetime τ_{fluo} strongly depends on detection wavelength. However, one has to consider that, for obtaining better time resolution, a prism monochromator was used with a transmission bandwidth of about 6 nm. The wavelengths given in Figs. 7 and 8 therefore are mean values and the decay times represent average values over an energy range of about 170 cm^{-1}. Figure 8 shows the wavelength dependence of the ratio $\tau_{\mathrm{fluo}}/\Phi^{\mathrm{rel}}_{\mathrm{fluo}}$ at 1.5 and 80 K and the aggregate emission spectrum at 5 K. We want to point out that the observed wavelength dependence is not, as one could think, due to the two different fluorescence bands, as the same dependence was observed for samples showing resonance fluorescence only.

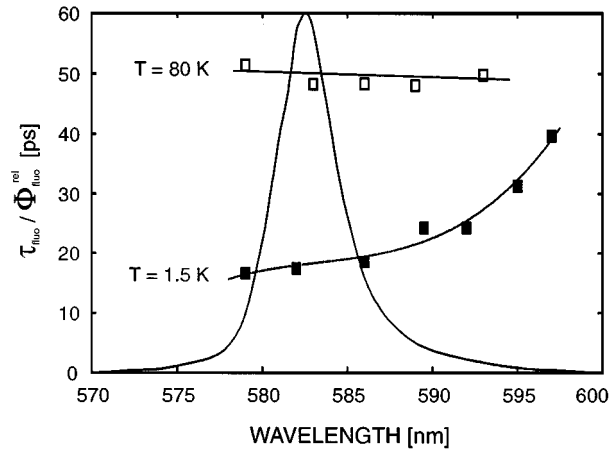

FIG. 8. Wavelength dependence of the fluorescence lifetime τ_{fluo} divided by the relative fluorescence quantum yield $\Phi^{\mathrm{rel}}_{\mathrm{fluo}}$ of TDBC *J* aggregates at 1.5 K (■) and at 80 K (□) (solvent: 1:1 mixture of ethylene glycol and water, concentration: 9×10^{-5} mol/ℓ). The spectrum is the resonance fluorescence of the sample at 5 K. Lines are guides to the eye.

The fluorescence decays were fitted with the sum of two exponentials where the long component of several hundred picoseconds had a very low amplitude (less than 1% contribution to the total integrated intensity) but was necessary in most cases for obtaining good fits. It is noteworthy that for the samples showing only resonance fluorescence a purely monoexponential decay was observed, indicating that the long decay time is connected to the appearance of the off-resonance fluorescence. For the discussion of the aggregate dynamics, we restrict ourselves to the short component.

The measured fluorescence lifetime τ_{fluo} (Fig. 7) in the temperature range below 40 K does not depend on temperature for any detection wavelength. Between 40 and 70 K, the lifetime changes with temperature and for the longer wavelengths it decreases with increasing temperature. Above 70 K, the lifetime increases with temperature for all wavelengths and, at about 80 K, the wavelength dependence of τ_{fluo} disappears. The temperature dependence of the fluorescence lifetime between 40 and 70 K (Fig. 7) may be an indication for an equilibration of the exciton over all thermally accessible states, causing the long (short) lifetimes to get shorter (longer).

An explanation for the wavelength dependence of the fluorescence lifetime is that at low temperature, relaxation processes within the exciton band become slow and have transition rates of the same order of magnitude like the decay to the ground state. At low temperatures, where there is very little thermally induced excitation to higher exciton states, this leads to a wavelength dependent lifetime first by depopulation of the higher excited states (by intraband relaxation at a rate comparable to the one of the direct decay to the ground state) and second, due to the same process, by a filling of the lower levels in the exciton band. At higher temperatures, this effect is compensated by thermally induced intraband excitation. In other words, the measured decay rates not only contain transitions from the exciton band to the ground state or a triplet state, but also intraband transitions. These different contributions cannot be distinguished in fluorescence lifetime experiments.

This explanation is supported by the static fluorescence emission spectrum which, below 80 K, actually shifts to the red by about 15 cm^{-1} with decreasing temperature, indicating that at low temperature most of the observed fluorescence comes from the lowest energy levels in the exciton band. Additionally, the decrease of the linewidth of the fluorescence emission is greater below than above 80 K, decreasing from about 170 cm^{-1} at 80 K to 125 cm^{-1} at 5 K. This indicates that at 5 K the emission comes from a smaller section at the bottom of the exciton band. The decrease in linewidth of about 45 cm^{-1} almost equals the difference in thermal energy between 80 and 5 K (75 K correspond to 52 cm^{-1}). Also, this concept is supported by the above-mentioned broad feature (marked II in Fig. 5) observed in the two-color pump–probe experiments when exciting in the high energy tail of the *J* band. The conclusion from this idea is that the observed dependence of the fluorescence lifetime on the detection wavelength is caused by intraband relaxation rather than by a change in the radiative lifetime as a function of wavelength.

It needs to be pointed out that the aforementioned intraband relaxation processes do not have to occur in one single exciton band, but relaxation by energy transfer between different aggregates may occur. In order for such an energy transfer between different aggregates (or better: coherence domains) to be efficient at low temperatures, the participating coherence domains should be located on the same chain of molecules. Such an interaggregate energy transfer has earlier been suggested by Sundstroem *et al.*[26] in order to explain the big differences between the aggregate sizes determined by exciton annihilation curves and spectral analysis.

A wavelength dependence caused by relaxation from exciton bands of different *J* aggregates to their respective ground states, without energy transfer between them, seems unlikely because one expects the aggregates with the lower energy exciton band (and thus with the larger redshift from the monomer transition) to be the larger ones, which in turn means that their fluorescence lifetime is expected to be shorter. This is in contradiction to the experimental results which show the opposite dependence.

Assuming an intermediate fluorescence lifetime in the *J* band of 25 ps at 1.5 K, a monomer radiative lifetime of 2.4 ns (from a Strickler–Berg analysis), and a low temperature aggregate size of 30 and 45 molecules, as obtained from the pump–probe experiments, one can calculate the radiative lifetime of TDBC *J* aggregates to be between 65 and 100 ps and the absolute fluorescence quantum yield to be between 25% and 40% (at 1.5 K). This is higher than the values of 21% and 8% found for the two *J* bands of PIC-Cl, respectively.[43] Using the aggregate size $N \approx 16$ for TDBC at room temperature,[36] the radiative lifetime at room temperature is expected to be about two to three times the one at low temperature, i.e., between 120 and 280 ps. Calculating the room temperature radiative lifetime directly from the 2.4 ns monomer radiative lifetime and the aggregate size of 16 molecules leads to an aggregate room temperature radiative lifetime of 185 ps, so the different experiments on TDBC *J* aggregates are consistent with each other. Using the absolute fluorescence quantum yield of 26% for TDBC *J* aggregates (in aqueous solution) at room temperature,[31] our values indicate a fluorescence lifetime of the TDBC *J* aggregates at room temperature between 31 and 73 ps which, in turn, is in good agreement with the directly measured value of 74 ± 5 ps[31] (measured by single-photon-counting experiments in aqueous solution).

A similar wavelength dependence of the fluorescence lifetime as observed for TDBC was recently reported for the *N*,*N*′-di(3-sulfopropyl) version of TDBC (called BIC).[46] However, the lifetime was only measured at two wavelengths at 4.5 K. The temperature dependence of the fluorescence lifetime reported for BIC[45] seems to be very different from the one measured for TDBC, strongly decreasing with increasing temperature in the range between 4 and 100 K. The lifetime at 4 K is three to five times longer than the lifetime we measured for TDBC (depending on wavelength). Also, no shift of the fluorescence emission (shifted about 10 nm to the

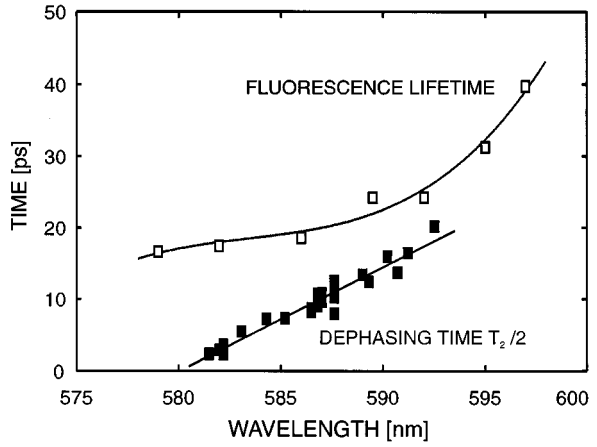

FIG. 9. Wavelength dependence of the fluorescence lifetime (□) and the phase relaxation time T_2 (■) of TDBC *J* aggregates at 1.5 K (solvent: 1:1 mixture of ethylene glycol and water; concentration: 9×10^{-5} mol/ℓ). Lines are guides to the eye.

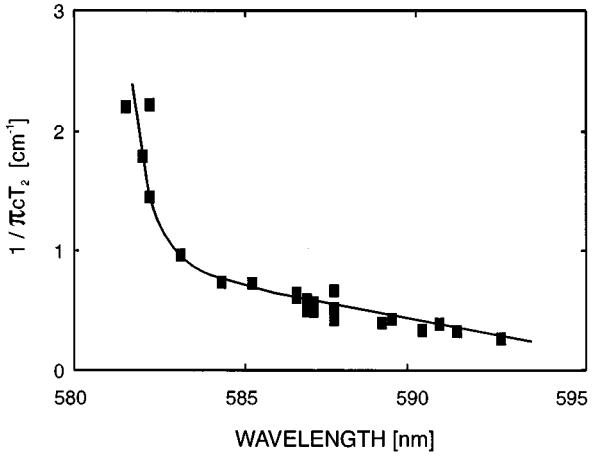

FIG. 10. Wavelength dependence of the homogeneous linewidth $(\pi cT_2)^{-1}$ in the TDBC *J* band at 1.5 K (solvent: 1:1 mixture of ethylene glycol and water; concentration: 9×10^{-5} mol/ℓ). The line is a guide to the eye.

red at room temperature compared to TDBC) was observed for BIC between room temperature and 4 K. It is remarkable that a small variation in a substituent causes such big differences.

The temperature dependence of the fluorescence lifetime of TDBC (Fig. 7) is quite similar to the behavior reported for PIC[8] and can be explained by the same effect for both dyes, an increasing exciton-phonon coupling with increasing temperature.

D. Exciton dephasing

The wavelength dependence at 1.5 K of the measured dephasing time T_2, obtained from the accumulated photon-echo experiments, is shown in Fig. 9 together with the corresponding fluorescence lifetimes at that temperature. The dephasing time T_2 decreases with decreasing measuring wavelength. Such dispersive dephasing in excitonic systems was previously observed by Tilgner *et al.*[47] for polysilane and by Fidder[43] for a thiacarbocyanine dye (TC). We also note that the echo decays can well be fitted with a single exponential, indicating that the observed wavelength dependence is not caused by the superposition of different processes.

If fluorescence was the only T_{1^-} (population relaxation) process, the observed wavelength dependence of the fluorescence and dephasing times would imply that the pure dephasing rate $1/T_2^*$ is much larger at higher energies [Eq. (5)]. Because one expects the pure dephasing to disappear at low temperature, this is an evidence that there are more T_{1^-} processes besides regular fluorescence and intersystem crossing. This confirms the earlier stated hypothesis of intraband transitions, which also contribute to the dephasing time measured in the echo experiments.

From the measured phase relaxation times one can calculate the homogeneous linewidth $(\pi cT_2)^{-1}$. The wavelength dependence of the homogeneous linewidth at 1.5 K (Fig. 10) is similar to the one reported by Fidder[43] for TC. It increases strongly at higher energies in the exciton band. In the case of TC, this dependence could be modeled assuming linear exciton–phonon scattering. In the case of TDBC, we attribute the dispersion of both the fluorescence and the photon echo decay times to intraband relaxation.

The temperature dependence of the homogeneous linewidth at 587 nm (red wing of the *J* band) is shown in Fig. 11. It increases about linearly in the investigated temperature range from about 0.5 cm^{-1} at 1.5 K to 1.5 cm^{-1} at 40 K. This increase of the homogeneous linewidth agrees with previously published results for the *J* aggregates of PIC and TC[43] and we conclude that this effect is caused by linear exciton–phonon scattering. However, the temperature region in which the experiments were done was limited because at temperatures above 40 K, the dephasing times were too short to be measured with the described experimental setup.

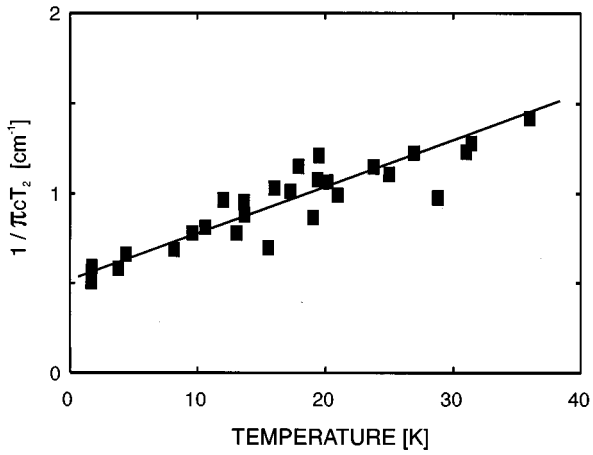

FIG. 11. Temperature dependence of the homogeneous linewidth $(\pi cT_2)^{-1}$ in the TDBC *J* band at 587 nm (solvent: 1:1 mixture of ethylene glycol and water; concentration: 9×10^{-5} mol/ℓ). The line is a guide to the eye.

V. SUMMARY

We have investigated the dynamics of the excitonic state of the *J* aggregating dye 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-di(4-sulfobutyl)-benzimidazolocarbocyanine (TDBC) by temperature and wavelength dependent measurement of phase and population relaxation times. Experimentally, this was done by time-correlated single-photon-counting and accumulated photon-echo experiments. Also, the temperature dependence of the fluorescence quantum yield and the two-color pump–probe spectra at 1.5 K were measured.

We found the temperature dependence of the fluorescence quantum yield to be equal to the one previously found for pseudoisocyanine (PIC). At temperatures below 80 K, a dependence of the fluorescence lifetime on detection wavelength was observed, with longer lifetimes at larger wavelengths. This effect is explained by intraband relaxation in the exciton band which, at low temperatures, is not compensated by thermally induced excitation to higher levels in the exciton band. This explanation is supported by the static fluorescence emission spectra. The intraband relaxation can also be interpreted in terms of relaxation between different exciton bands (of different aggregates), which relies on the possibility of energy transfer between different coherence domains on the same physical chain of dye molecules. The measured temperature and wavelength dependence of the dephasing qualitatively is similar to the one previously reported for other *J* aggregating dyes like PIC and TC. We conclude that intraband relaxation is responsible for the optical response of TDBC in the single-photon-counting and photon-echo experiments. Using a model of motional narrowing for disordered molecular aggregates, extended to include intersite correlation, the two-color pump–probe experiments indicate a high correlation of the transition frequencies in a TDBC *J* aggregate. From the pump–probe experiments, a size of the coherence domain of TDBC *J* aggregates between 30 and 45 molecules at 1.5 K is determined. This result is consistent with results from fluorescence lifetime experiments and from other *J* aggregating dyes. Using this aggregate size and the monomeric radiative lifetime of 2.4 ns (from a Strickler–Berg analysis) the absolute fluorescence quantum yield is determined to be between 25% and 40% for TDBC *J* aggregates in a 1:1 ethylene glycol/water mixture at 1.5 K.

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